

Ion-induced chemical vapor deposition of copper films with nanocellular microstructures

F. Ross,^{a)} C. V. Thompson, and T. Chiang^{b)}

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

H. H. Sawin

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 19 March 2003; accepted 6 June 2003)

Ion-induced chemical vapor deposition using a broad ion beam has been used to deposit nanocellular films. These films consist of closely packed 10–20 nm diameter copper rods separated by a carbonaceous residue, and growing in a direction normal to the substrate surface to lengths equal to the film thickness. The effects of ion flux, ion energy, and substrate temperature on rod spacing were investigated. A growth mechanism analogous to that leading to cellular structures during solidification from alloy melts is proposed and qualitatively described. Films with nanocellular structures are expected to have useful, highly anisotropic properties. © 2003 American Institute of Physics. [DOI: 10.1063/1.1599964]

Ion-induced chemical vapor deposition (II-CVD) with focused ion beams is used to deposit metal lines and other features for circuit and x-ray mask repair.^{1,2} II-CVD typically involves the use of a metalorganic precursor delivered to a substrate that is held at a temperature below the temperature required for pyrolysis. The ion flux provides the extra energy that causes localized decomposition of the adsorbed precursor and deposition of a metal film.³ This often leads to the incorporation of carbonaceous impurities, especially at low substrate temperatures.^{3–6} High purity metallic films can be obtained by depositing under conditions for which the carbonaceous reaction products that result from the physical processes are volatile. Depositing at temperatures almost as high as those required for pyrolytic deposition leads to higher purity,⁷ whereas flooding the reaction surface with a reactive H-atom beam at lower temperatures essentially eliminates the carbonaceous impurity.⁸ In this letter we describe the discovery that when II-CVD is purposely carried out under conditions in which both metal and non-volatile carbonaceous byproducts are deposited, a nanocellular growth process can result in the growth of self-assembled tightly packed arrays of nanowires.

In this and an earlier study,⁶ copper(I) hexafluoroacetylacetonate-vinyltrimethylsilane [copper (I)hfacVTMS] was used as a metalorganic precursor and II-CVD was carried out using a 1000 eV Kaufman Ar⁺ broad beam ion gun in a custom built vacuum system with a base pressure below 4×10^{-8} Torr. Deposition rates were monitored using a quartz crystal microbalance prior to and after a deposition. Deposition was carried out on commercially available amorphous carbon substrates for use in plan-view transmission electron microscopy (TEM), and on surface oxidized oxygen-free high conductivity copper substrates for

cross-sectional transmission electron microscopy samples. It was demonstrated in earlier experiments that deposition on Si₃N₄-coated Si and a variety of other substrates yields the same microstructures, indicating that the observed microstructure development is not influenced by the choice of substrate.

An example of the nanowire array structures obtained in a range of deposition conditions is shown in plan view in Fig. 1(a) and in cross section in Fig. 1(b). This was deposited at 25 °C using 500 eV ions at a flux of 10.6 $\mu\text{A}/\text{cm}^2$ and with a local copper(I)hfacVTMS pressure of about 0.5 mTorr. The film consists of high-aspect-ratio 14–15 nm diameter copper columns embedded in, and separated by, a matrix of carbonaceous residue. Column diameters were uniform over the roughly 1 mm² TEM sample area. The columns grow in a cellular fashion with axes perpendicular to the plane of the substrate.

We have investigated the effects of growth rate, growth temperature, and ion flux on the characteristics of nanocellular structures. All experiments were carried out in the ion-flux-limited regime in which the growth rate is proportional to the ion flux. In one set of experiments, the ion energy was fixed but the growth rate (by varying the ion flux, see Table I) and deposition temperature (25–100 °C) were varied [Fig. 2(a)]. In a separate set of experiments, the ion beam voltage and the deposition temperature was varied while the film growth rate was kept constant at 0.3 Å/s [Fig. 2(b)]. Film structures were characterized using TEM, and the average column diameter was characterized using a technique based on metallographic principles originally formulated by Fullman.⁹

X-ray photoelectron spectroscopy (XPS) compositional analysis on the TEM samples indicated, for example, that the copper atomic percent fraction ranged from 85% to 70% when the deposition rate was increased from 0.1 to 0.5 Å/s (the ion flux increasing from 1.4 to 10.6 $\mu\text{A}/\text{cm}^2$) at 25 °C. Selected area diffraction during TEM imaging was used to

^{a)}Present address: P.O. Box 2266, Merrifield, VA 22116-2266; electronic mail: flr22@columbia.edu

^{b)}Also at: Angstrom Systems, 3350 Scott Blvd. #62, Santa Clara, CA 95054.

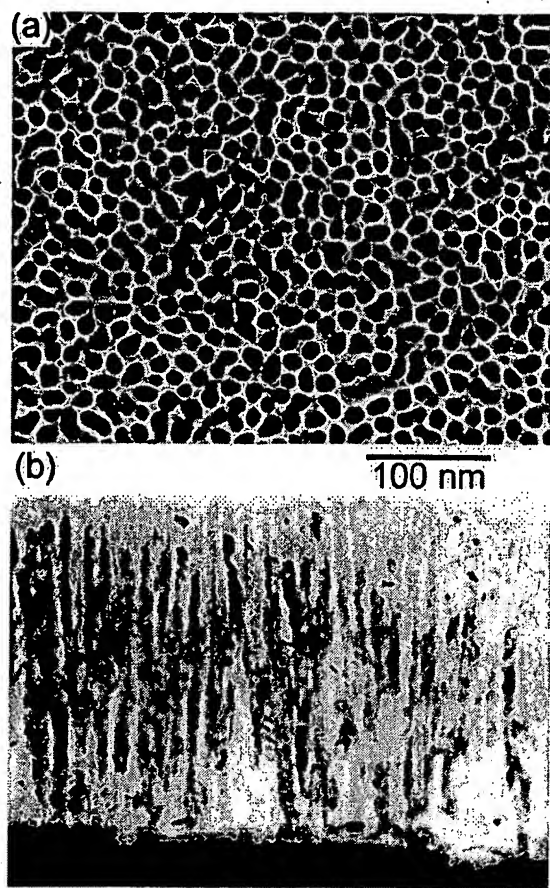


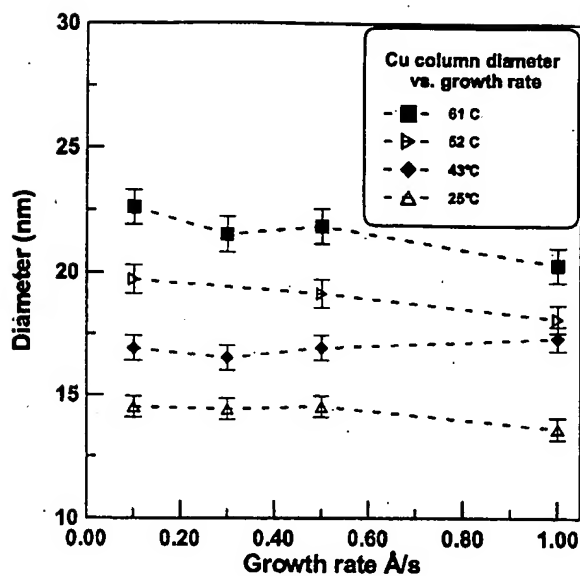
FIG. 1. Nanocellular microstructure obtained through II-CVD of copper using copper(I)hexafluoroacetylacetonate-vinyltrimethylsilane at 25 °C and 500 eV argon ions at a flux of $10.6 \mu\text{A}/\text{cm}^2$. The plan view sample (a) is 500 Å thick. The cross-sectional sample (b) shows that the films are composed of high-aspect-ratio copper columns.

verify that the dark columns in the microstructure could be indexed as copper. Scanning TEM (STEM)-energy dispersive spectroscopy (EDS) maps also confirmed that the columns were copper. STEM-EDS with 1 nm resolution was used for characterization of the material between the columns, and indicated that C was the primary detectable constituent. However, the intracolumnar copper content increased with decreasing growth rate.

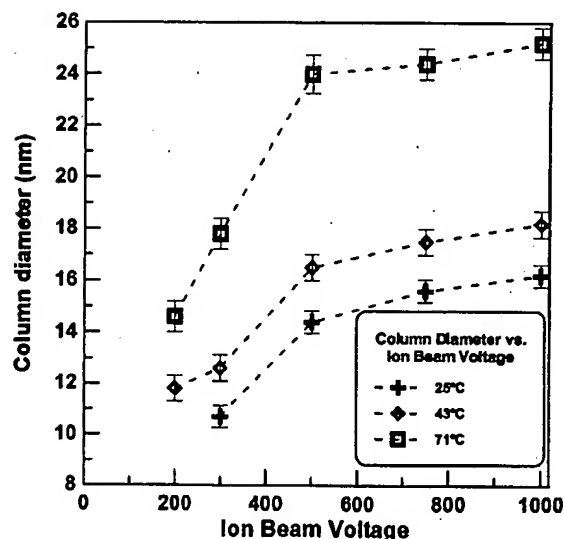
Deposition at temperatures between 60 and 100 °C also lead to nanocellular microstructures, although without the regularity of the lower temperature depositions. However, it is noteworthy that the nanocellular microstructure was retained at 100 °C where the carbon fraction was roughly 1

TABLE I. Ion fluxes and deposition rates for data in Fig. 2.

25 °C and 500 V ion beam	Rate (Å/s)	0.1	0.3	0.5	1.0
	Ion flux ($\mu\text{A}/\text{cm}^2$)	1.4	5.85	10.6	21.6
43 °C and 500 V ion beam	Rate (Å/s)	0.11	0.29	0.52	1.0
	Ion flux ($\mu\text{A}/\text{cm}^2$)	1.4	5.5	11.3	24.1
52 °C and 500 V ion beam	Rate (Å/s)	0.1	0.5	1.1	
	Ion flux ($\mu\text{A}/\text{cm}^2$)	1.1	12.3	21.7	
61 °C and 500 V ion beam	Rate (Å/s)	0.1	0.3	0.5	1.0
	Ion flux ($\mu\text{A}/\text{cm}^2$)	1.2	2.4	9.6	19.5



(a)



(b)

FIG. 2. (a) Column diameter vs growth rate in the ion-flux-limited regime for a 500 eV ion beam voltage. (b) Column diameter vs ion beam voltage at three different process temperatures but a constant growth rate of 0.3 Å/s.

at. %, or at the approximate detection limit using XPS. Only a H-atom assisted deposition, which removed all carbon within the detection limit of XPS, produced a noncolumnar equiaxed microstructure.

The data in Fig. 2 indicate that the cell spacing for these nanocellular structures is at best weakly growth rate dependent, but increases with both increasing deposition temperature and increasing ion energy. The chemical analyses suggest that pure copper islands nucleate and grow as rods that are surrounded by nonvolatile carbonaceous fragments of the metalorganic precursor. We postulate that these nonvolatile fragments are "rejected" at the surface of the growing copper nanorods, and are transported laterally on the surface of the growing film, to segregate between the growing copper rods (see Fig. 3). The distance of this lateral transport then

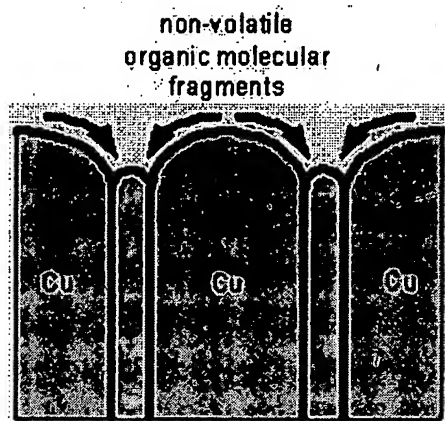


FIG. 3. Sketch illustrating the proposed mechanism leading to the development of nanocellular microstructures during II-CVD.

governs the rod spacing. Note that the matrix will accommodate "excess" copper when the growth rate is slow and the nominal macroscopic copper fraction is higher.

This process is analogous to cellular growth that often occurs during solidification from alloy melts.¹⁰ In liquid-phase cellular growth, the transport distance of rejected impurities also governs the cell size/spacing. However, in liquid-phase cellular growth, the cell size decreases with decreasing growth rate (roughly linearly), unlike the present case of II-CVD cellular growth. In the II-CVD process, the lateral transport distance may be a function of ion-assisted

diffusion distances on the surface of the growing film. This distance depends on temperature, as well as the energy and flux (number per unit area, per unit time) of the incident ions, but not separately on the growth rate.

In conclusion we have demonstrated the possibility of growing controlled nanocellular microstructures using a low voltage broad ion beam at or near ambient temperatures. Films with such nanocellular structures are expected to have highly anisotropic properties. It is possible that other metallic nanostructures with specific functionality could be deposited using other precursors with the appropriate chemistry.

This work was supported by the National Science Foundation.

- ¹J. Orloff, L. Swanson, and M. Utlaut, *High Resolution Focused Ion Beams: FIB and Applications* (Kluwer Academic, Dordrecht, 2002).
- ²H. C. Petzold and P. J. Heard, *J. Vac. Sci. Technol. B* **9**, 2664 (1991).
- ³A. D. Dubner and A. Wagner, *J. Appl. Phys.* **66**, 870 (1989).
- ⁴J. S. Ro, C. V. Thompson, and J. Melngailis, *J. Vac. Sci. Technol. B* **12**, 73 (1994).
- ⁵J. S. Ro, C. V. Thompson, and J. Melngailis, *Thin Solid Films* **258**, 333 (1995).
- ⁶T. P. Chiang, H. H. Sawin, and C. V. Thompson, *J. Vac. Sci. Technol. A* **15**, 3104 (1997).
- ⁷P. G. Blauner, Y. Butt, J. S. Ro, C. V. Thompson, and J. Melngailis, *J. Vac. Sci. Technol. B* **7**, 1816 (1989).
- ⁸T. P. Chiang, H. H. Sawin, and C. V. Thompson, *J. Vac. Sci. Technol. A* **15**, 2677 (1997).
- ⁹R. L. Fullman, *J. Met.* **5**, 449 (1953).
- ¹⁰M. C. Flemings, *Solidification Processing* (McGraw-Hill, New York, 1974).